Bay Area Air Quality Management District

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Workshop Staff Report

September 27, 2005

Further Study Measure 9
Refinery Wastewater Treatment Systems

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WORKSHOP STAFF REPORT
Further Study Measure 9:
Refinery Wastewater Treatment Systems

I. INTRODUCTION

A. Summary of Proposal

The Bay Area Air Quality Management District (District) does not expect to amend further its rules and regulations concerning refinery wastewater collection and separation systems (Regulation 8, Rule 8) at this time. This Workshop Report explains the District's determination.

B. Background

Each of the five Bay Area refineries has a system that collects and treats wastewater from refinery processes and operations prior to discharge as effluent into San Francisco Bay Area waters. Each refinery has similar or some of the same treatment components as those of another refinery, but no two refinery wastewater collection and treatment systems are identical.

In 2001, the District adopted the Revised San Francisco Bay Area 2001 Ozone Attainment Plan to attain the national one-hour ozone standard (the 2001 Plan). At that time, the District lacked adequate data to determine whether the imposition of controls or adoption of more stringent standards on then-uncontrolled components of a petroleum refinery's wastewater system would reduce volatile organic compound (VOC) emissions significantly at each of the five refineries. Therefore, the 2001 Plan included a commitment to examine whether there were significant potential VOC emission reductions achievable from controlling refinery wastewater collection and treatment system components (Further Study Measure 9, "Refinery Wastewater Treatment Systems"). The District, jointly with the California Air Resources Board (CARB), undertook a two-phase study to investigate the wastewater collection and treatment systems of the five refineries.

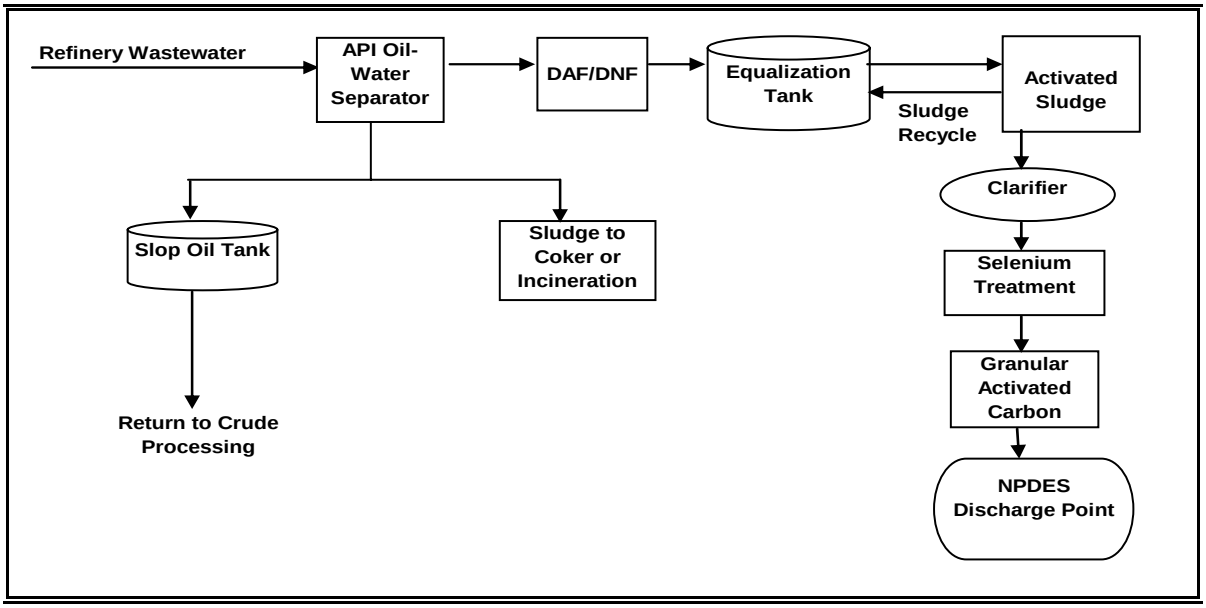
The District completed the first phase of the study in 2004, focusing primarily on wastewater collection systems. On September 21, 2004, the District amended Regulation 8, Rule 8 to impose, among other measures, a more stringent vapor leak standard of 500 parts per million (ppm) on controlled wastewater collection system components and oil-water separators and the requirement of a wastewater collection system inspection program. The District estimates the September 2004 amendments to Regulation 8, Rule 8 will reduce VOC emissions by 2.1 tons per day (tpd).

The District has now completed the study's second phase, an investigation of whether there are potential significant VOC emission reductions to be achieved from control of the refineries' secondary wastewater treatment components. The results of this study are the basis for the District's decision not to amend Regulation 8, Rule 8 further at this time.

II. PETROLEUM REFINERY WASTEWATER SYSTEMS

Each Bay Area petroleum refinery has a system of drains and piping to collect wastewater from the refinery processing units and other operations and transport the influent to the primary and secondary treatment units. The treated effluent must meet all applicable California Regional Water Quality Control Board standards prior to discharge into bay waters. Figure 1 shows a simplified refinery primary and secondary wastewater treatment system. Each of the refineries has a unique combination and configuration of the treatment processes shown in Figure 1.

Figure 1: Simplified Refinery Wastewater Treatment System



Source: US EPA

Primary treatment consists of oil-water separation and dissolved nitrogen flotation (DNF) or dissolved air flotation (DAF) units. An oil-water separator removes solids, oil and other petroleum products from the influent. DAF/DNF units remove organic materials from the stream. Three refineries have enclosed DNF units (as required by Rule 8-8-305) in which VOC emissions are controlled by a vapor recovery system. One refinery does not operate a DAF or DNF unit. Another refinery has an enclosed DAF unit with four vents to atmosphere and effluent is transported from the DAF to the biological treatment unit through a grated channel and a weir (channel/weir). At the other refineries, the wastewater is piped from the separation or gas flotation devices to the biological treatment units.

At secondary treatment, the wastewater undergoes biological treatment in either large, open and bermed aerated ponds and lagoons (at two refineries) or in constructed activated sludge tanks (at two refineries). One refinery has two biological treatment units that include an activated sludge tank and an aerated pond. These units are all open to the atmosphere. Microorganisms feed on, and remove, the majority of organics from the wastewater. Additional secondary treatment processes include flow controls, pH balancing, and the addition of chemicals and nutrients to protect the bacteria.

Volatilization and hydrocarbon stripping generate most of the VOC emissions to the atmosphere during wastewater treatment. Volatilization occurs in open tanks, ponds, and the channel, when the petroleum in wastewater is exposed to the atmosphere. Stream turbulence strips hydrocarbons from the wastewater. Turbulence occurs in one refinery's weir and from mechanical agitation during biological and activated sludge treatment at all refineries. The composition of the wastewater contaminants, the wastewater temperature, and the treatment units' particular design affect the extent of volatilization and stripping emissions.

III. Summary of Technical Review

A. Evaluation and Quantification of VOC Emissions

The District estimates a total of 0.24 tons per day (tpd) of VOC emissions from the uncontrolled secondary treatment units located at the five refineries and the DAF unit and channel/weir at one refinery, ConocoPhillips. Of that total, the DAF unit and channel/weir at ConocoPhillips contributes more than 40 percent of the estimated total VOC emissions (0.1 tpd) from all five refineries. Table 1 presents a summary of the VOC emission estimates.

District and CARB staff estimated the VOC emissions of the channel/weir and secondary treatment units for each refinery using the TOXCHEM+ modeling program (TOXCHEM+). The emissions from the DAF unit were measured by the District's source test team. TOXCHEM+ provides a comprehensive evaluation of the fate of multiple organic compounds in wastewater during treatment. It is approved by the United States Environmental Protection Agency (EPA).

The District developed a refinery-specific treatment process diagram in TOXCHEM+ to simulate current conditions at each refinery. The District calibrated the model (using EPA-approved flux chamber technology) based on direct vapor measurements from the ConocoPhillips and Valero refineries. The District collected wastewater grab samples at the point of entry to each refinery's biological treatment unit and at the point of discharge into bay waters to further refine the model for each refinery. The model calculated potential emissions from each secondary treatment unit at each refinery, using a single gasoline-range compound that was representative of each refinery's wastewater stream components.

Modeling has inherent inaccuracies in estimating the emissions of specific processes because mathematic equations are used to approximate real life conditions. For example, the model computes a single concentration value for a component, but actual concentrations and emissions vary temporally, spatially, and seasonally. The District calibrated the model based

on limited direct vapor measurements that were collected from a single day of sampling. EPA has determined that the accuracy of the flux chamber sampling test method to collect direct vapor measurements is +/-30%. Further adjustments to the model can affect the total estimated VOC emissions by +/-15% which is within the accuracy of the flux chamber test method. Such adjustments include inclusion of other compounds or using an alternative fate and transport model. These adjustments introduce additional uncertainty.

At four of the refineries, most VOC emissions occurred in the biological treatment units or activated sludge units as a result of turbulent conditions. At the fifth refinery, the DAF vents and channel/weir were the major sources of VOC emissions. The vents release organic compounds to the atmosphere, and VOCs volatilize from wastewater in the channel or are stripped from the stream in the weir. The District collected source test samples from each of the vents. VOC emissions were estimated by summing the individual non-methane hydrocarbon concentrations and multiplying this total VOC concentration by the flow rates measured at each vent.

The open equalization ponds and clarifiers, which follow biological treatment units at all of the refineries, had negligible or minimal emissions.

Table 1: VOC Emission Estimates for Refinery Wastewater Treatment Units

Refinery	DAF Vents (tpd)	Effluent Channels/ Weir (tpd)	Biological Treatment Units (tpd)	Equalization Ponds and Clarifiers (tpd)	Total Estimated VOC Emissions (tpd)
ConocoPhillips	0.083	0.022	0.0026	*	0.108
Shell	n/a	n/a	0.023	0.00040	0.023
Tesoro	n/a	n/a	0.049	*	0.049
Valero	n/a	n/a	0.023	*	0.023
Chevron	n/a	n/a	0.033	*	0.033
TOTAL	**0.083**	**0.022**	**0.131**	**0.0004**	**0.236**

Note:
n/a: not applicable, these units are not presented at the refinery
*: the model estimated negligible emissions from these process units

B. Identification and Evaluation of Potentially Available Controls

The District investigated the technical feasibility, potential emission reductions, and cost of several approaches to reduce VOC emissions from the secondary treatment processes and from the ConocoPhillips DAF vents and channel/weir. These approaches either remove VOCs from the wastewater stream prior to its entry to secondary treatment or reduce the stream's exposure to the atmosphere. The District estimated a total annual cost (over ten years), which was comprised of the annualized capital costs and annual recurring operation and maintenance costs. The range of total costs reflects the variability of the volume of flow a refinery treats. Emission reductions were estimated by multiplying the total VOC

emissions from the biological treatment units and channel/weir by the average removal efficiency estimated for each control technology.

Steam stripping is a proven technology to remove VOCs prior to secondary treatment. It requires proper venting to a secondary control device and monitoring to insure optimal operation. The District estimates that the total cost to install, inspect and maintain a steam stripper at each refinery over a ten-year period ranges between $7.1 million and $17.9 million. Estimated VOC emission reductions are 0.14 tons per day (tpd) based on a 90% removal efficiency if the steam stripper is installed to treat wastewater that enters the biological treatment unit and channel/weir.

Liquid phase carbon adsorption may be used as a stand alone control device, but is also suitable as a secondary control device to reduce VOC emissions from gas phase vent streams from a steam stripper. The District estimates that the total annual costs are comparable to that of a steam stripper. The District estimates VOC emission reductions to be 0.14 tpd based on a 90% removal efficiency. Total annual costs for this technology are estimated to be $6.7 million to $24 million. A number of factors may limit the equipment's effectiveness. For example, high suspended solids and oil and grease can foul the carbon and require extensive pretreatment. Refineries must continuously monitor the equipment to ensure that the carbon beds are regenerated.

Two refineries have activated sludge tanks that may accommodate domed aluminum roofs to contain VOC emissions. The District assumed a 95% VOC removal efficiency and estimated a total of 0.025 tpd reductions from the two refineries' activated sludge units. The District estimated that the total cost to install, operate and maintain the aluminum domes over a ten-year period would range from $100,000 to $900,000 at the two refineries. This estimated cost does not include additional expenses to install and operate VOC abatement equipment. For example, each refinery will have to install vapor recovery units and replace the existing microorganisms with those that can survive under dark conditions. As noted above, two refineries have bermed aeration lagoons and ponds that cannot accommodate a dome. These refineries would have to install foundations and support structures to contain them or replace the lagoons and ponds with tanks. For one of the refinery that has both a tank and pond treatment system, the cost associated with doming the single tank was not evaluated since the majority of the emissions from the secondary treatment process was associated with the aerated pond.

IV. Summary of Public Consultation Process

The upcoming October 27, 2005 public workshop is the latest step in the District's consultation with members of State agencies, industry, environmental organizations and the public as part of its evaluation of whether to amend this Rule. Following the public workshop, District staff will prepare a final proposal and present it at a public hearing of the District's Board of Directors. The District anticipates a public hearing on December 7, 2005.

A. Technical Workgroup Meetings

The District and CARB formed the Refinery Wastewater Technical Working Group in 2002 to assist in the two-phase evaluation of the refineries' wastewater treatment systems and potential amendments of Regulation 8, Rule 8. The Group consists of representatives of the Western States Petroleum Association, the five Bay Area refineries, a consultant from Brown and Caldwell, Communities for a Better Environment, CARB, District staff and Charles Schmidt, the District's sampling and emissions modeling contractor. The District convened meetings on April 4, June 8, and September 14, 2005, as well as conference calls, to discuss the Phase Two Work Plan, proposed emissions model and sampling plan and methodology.

B. Public Workshop

The District is holding this public workshop to solicit comments from the public on the District's current determination not to amend Regulation 8, Rule 8 at this time. The District will also respond to questions about information set forth in this Workshop Staff Report. District staff will incorporate responses to public comments in the Staff Report to be presented to the District's Board of Directors at a public hearing.

V. Explanation for Not Proceeding with Rule-Making at this Time

District staff has determined that at this time, the estimated emissions reductions of 0.14 tpd to be achieved from additional controls of refinery wastewater treatment systems do not warrant additional amendments to Regulation 8, Rule 8 given the present cost of implementing the known control technologies. This determination does not preclude District staff from revisiting the imposition of further controls on refinery wastewater treatment systems in the future or reducing emissions using other measures such as permitting actions.